

Using Block Copolymers in Nanostructured Architectures in Lithium Batteries

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The ideal electrolyte material for a solid-state battery would have the ionic conductivity of a liquid, the mechanical properties of a solid, and the formability of a commodity thermoplastic. In this laboratory it has been shown that this challenge can be met with a class of polymers known as block copolymers [1]. Block copolymers consist of two chemically dissimilar polymers covalently bonded end-to-end. Under appropriate conditions, a net repulsion between the polymer blocks induces their local segregation, or “microphase separation”, into periodically-spaced nanoscale domains. By choosing a lithium salt-solvating polymer as one block component, continuous ion-conducting pathways can be formed. The nanoscale morphology confers solid-like mechanical properties to the material at macroscopic scales even if both polymer blocks reside well above their respective glass transition temperatures [2,3]. By choosing two low T_g , noncrystallizing blocks, films with mechanical properties similar to those of a crosslinked rubber can be obtained without sacrificing the high local chain mobility required for Li^+ conductivity. Because microphase separation is thermodynamically reversible with the addition of a common solvent, block copolymers can be readily processed by conventional polymer coating methods.

Proof of this concept has been demonstrated here in our laboratory with the copolymer of poly[oligo(oxyethylene) methacrylate] - *b* - poly(laurel methacrylate) [(POEM) - *b* - (PLMA)] which proved to be mechanically stable but exhibited nearly the same ionic conductivity as the molten POEM homopolymer [1]. With this copolymer serving as both the supporting electrolyte and the cathode’s binder, thin-film, solid-state, rechargeable lithium batteries of the type Li/BCE/LiMnO₂ have been constructed. These cells have been multiply cycled at room temperature. Additionally, Li/BCE/Al cells have been repeatedly cycled at temperatures as low as -20°C to demonstrate the utility of the BCE at subambient temperatures [1].

This block copolymer, sometimes with and sometimes without further tailoring, has demonstrated its utility in three different applications: (i) a high-conductivity, single-ion-conducting electrolyte, (ii) a self-organizing nanocomposite anode, and (iii) a thin-film microbattery.

(i) The goal here was to raise the transference number of Li^+ to nearly unity by tailoring molecular architecture. The strategy consisted of attempting to immobilize the counterions by tethering them to the polymer backbone. In this way, Li^+ is introduced not in the form of a soluble salt, e.g., LiCF_3SO_3 , but rather as part of the block copolymer. Thus, in a sense, these systems can be viewed as self-doped; accordingly, we have dubbed them self-doped block copolymer electrolytes (SDBCEs).

Preliminary work had identified a class of organic anions with very low charge density that might be suitable for this purpose. Upon copolymer ordering, these attached anions become sequestered within the secondary block nanodomains, while Li^+ ions are localized to the primary,

ionically-conducting block nanodomains. Binding the counterions should reduce their mobility substantially and result in a dramatic rise in t_{Li^+} , the Li^+ transport number.

In principle, it should be possible to raise the value of t_{Li^+} in this manner to 1, thereby making the material effectively a single-ion conductor.

(ii) In an attempt to design an anode that is both carbon-free and lithium-free yet capable of delivering high discharge currents (high rate capability), block copolymers were employed as templates for establishing and maintaining contact with a metallic dispersion of nanoparticles. To demonstrate proof of concept, gold was chosen as the metallic dispersion owing to its nobility (and hence its freedom from formation of an oxide surface film) and ability to alloy with lithium. The idea was to form gold nanoparticles in situ via metallothermic reduction of a gold-bearing salt which would dissolve in one of the domains of the block copolymer. Electrical contact with the gold dispersion was to be established by single walled carbon nanotubes (SWNTs) which also position themselves in the same domain of the block copolymer as does the gold salt. Furthermore, surface tension forces tend to keep both the gold particles and the carbon SWNTs as far from the domain boundary as possible. The consequence is to put the gold particles and the SWNTs in contact and to keep them that way.

(iii) For the operation of sensory enhancement equipment, communications systems, etc. portable electrical power is an essential element for marines in field operations. With projected practical energy densities exceeding 300 Wh/kg, low safety risks and great flexibility in battery configuration, the lithium polymer battery (LPB) is an attractive option for the distributed power storage needs of soldiers. For underwater missions the LPB has the added advantages of pressure tolerance and near neutral buoyancy. However, a number of materials and processing challenges must still be overcome to achieve these performance advantages. The purpose of the present study was to determine the performance limits of a thin-film battery comprising an additive-free (no carbon, no binder) oxide cathode, a solid polymer electrolyte, and a metallic lithium anode.

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